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An Inter-comparison Exercise on Evaluating the Application of Novel Techniques in Radiochemical Analysis

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Abstract

Effective sample processing techniques are essential in radionuclide determination for emergency preparedness, environmental monitoring, nuclear decommissioning and waste management to achieve expedite analysis. In 2014, NKS-B Rapid-Tech project gathered scientists working in radiochemistry among Nordic countries and oversaw the problems and needs in developing effective radiochemical methods. Based on screening the current analytical methods for common radionuclides (e.g., Sr, actinides) assays in individual institute, challenges and future development were identified by each institute. Several consensuses through the screening have been summarized in the final project report (NKS-336).
To practically evaluate the analytical benefit in application of novel sample processing techniques and to exchange experiences for improving radioanalytical methods used for different purposes in nuclear-related field, an inter-comparison exercise for determination of ^{90}Sr and Pu isotopes in environmental samples was performed in 2015 among the collaborative institutes. The results obtained from the inter-comparison exercise are evaluated and the analytical performance of different novel techniques are discussed and summarized in this report.

Key words

Novel techniques, radiochemical analysis, Pu, Sr, inter-comparison, soil, milk

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An Inter-comparison Exercise on Evaluating the Application of Novel Techniques in Radiochemical Analysis

Final report from the NKS-B Rapid-Tech activity

(Contract: AFT/B(15)6)

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To practically evaluate the analytical benefit in application of novel sample processing techniques and to exchange experiences for improving radio-analytical methods used for different purposes in nuclear-related field, an inter-comparison exercise for determination of ^{90}Sr and Pu isotopes in environmental samples was performed in 2015 among the collaborative institutes. The results obtained from the inter-comparison exercise are evaluated and the analytical performance of different novel techniques are discussed and summarized in this report.

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1. Introduction

Radiochemical analyses are important to provide analytical data for radionuclides that can be used in environmental risk assessment and monitoring, nuclear emergency preparedness, nuclear decommissioning and waste disposal, radioecology and tracer studies as well as nuclear forensics. For the various situations mentioned above, the method of choice are most likely different due to the different analytical purposes and different criteria of clearance limits. However, in all cases mentioned above, efficient analytical performance of the radiochemical method is desirable. As an ideal radio-analytical method, it should have both characters of high analytical quality and low analytical cost. The high analytical quality can be interpreted as sufficient low detection limit, high analytical accuracy/precision and high robustness of the method, while the low analytical cost should be related to low labor intensity, short analytical time and high sample throughput.

In recent year, novel and effective sample treatment technologies, automation of radio-analytical protocols and optimization of analytical protocols are becoming attractive to many researchers in the recent years to reduce analytical time and labor intensity (S. Holmgren *et al.* 2016, A. Tovedal *et al.* 2008, Ramebäck *et al.* 1994). Examples of novel techniques are flow-based fully automated methods such as flow injection (FI)/sequential injection (SI) and high performance liquid chromatography (HPLC) in combination with on-line inductively coupled plasma mass spectrometry (ICP-MS) detection, or semi-automated vacuum-box-integrated chromatographic separation, or other well-chosen, simple and effective sample decomposition approaches (e.g., microwave assisted digestion, alkaline fusion) as well as chemical purification techniques (precipitation, co-precipitation, chromatography etc.). Optimization of analytical protocols may include simplification of analytical protocol, reducing labor intensity and minimize measurement time (or time for daughter radionuclide ingrowth), provided that the optimized protocol still achieves requested analytical performances (e.g., limit of detection, accuracy and precision).

As of today, a few Nordic laboratories working with radiochemistry have initiated research and development in developing rapid radiochemical methods using different novel and effective sample treatment techniques. It should be noted herein that these ‘rapid methods’ are not restricted to the application in nuclear emergency preparedness which requires a fast data report, the methods are also applicable to all other situations including nuclear decommissioning, environmental monitoring and scientific studies in radioecology where efficient radiochemical analyses are needed. However, the exploration of novel techniques to achieve expedite analysis is still a fresh area, and their application in radio-analysis is probably hampered due to time and lack of continuity since it takes a considerable effort to get into and understand the various methods. To stimulate communication and to shed some light on such practical problems, an inter-comparison exercise for determination of ^{90}Sr and Pu isotopes in environmental samples was performed in 2015 within the NKS Rapid-tech project. This report summarizes the technical details of the inter-comparison exercise, as well as the overall results, discussion and perspectives achieved in this exercise.

2. Material and methods

2.1 Samples

Environmental soil and dry milk samples were used for the inter-comparison exercises. Two reference materials from a laboratory round-robin inter-comparison, a Danish soil and a

Syrian soil from the IAEA-TEL-2015 ALMERA proficiency test (soil no.5) were used for Pu isotopes determination. The Danish soil was the top 10 cm of 2 mm sieved soil from 12 different Danish locations collected during 2003 and pooled at Risø National Laboratory, Denmark (Roos *et al*. 2009). The soil was further sieved through 0.6 and finally through a 0.4 mm sieve and coarsely mixed by hand. Following a single homogenization of all soil for 30 minutes in a large volume mixer a total of 17 kg soil remained. The raw material of Syrian soil was collected and treated in Syria by the Syrian Atomic Energy Commission. After drying it was milled, sieved under the 90 micron, ashed at 650 °C, homogenised and packed into the plastic bottles. The packing unit contains 250 g of ash of soil. The sample is sterilised by 25 kGy gamma doses. The Syrian soil and one dry milk powder collected in June 2015 from Videbæk, Denmark were utilised for determination of ^{90}Sr. The detailed information of the sample is listed in Table 1.

2.2 Determination of Pu in soil samples

2.2.1 DTU-Pu-I method

10 g of soil was ashed at 550 °C overnight. About 10 mBq of ^{242}Pu was spiked to the sample as a chemical yield tracer. The sample was digested with 100 ml of aqua regia on a hotplate at 150 °C for 30 min and 200 °C for 2 h, respectively. After cooling, the sample was filtered through a GF/A filter. The beaker and the filter were washed with 30 ml of 0.2 mol/l HCl. The wash solution was combined with the filtrate. 2.5 mol/l $NH_3 \cdot H_2O$ was added to adjust the pH to 8-9. The supernatant was discarded after centrifugation and the residue was dissolved with 5 ml of 12 mol/l HCl. 300 mg of $K_2S_2O_5$ were added and the solution was stirred for 20 min. 2.5 mol/l $NH_3 \cdot H_2O$ was added to adjust pH to 9-10. The precipitate obtained after centrifugation was dissolved with 5 ml of 14 mol/l HNO_3. The sample solution was adjusted to 8 mol/l HNO_3 and loaded onto a 8-mL column (1.0 cm i. d. × 10 cm length) packed with AG 1× 4 resin (100-200 mesh, BioRad Laboriatories Inc., Hercules, CA). The column was rinsed with 200 ml of 1 mol/l HNO_3 followed by 100 ml of 9 mol/l HCl. Pu is finally eluted with 100 ml of 0.2 mol/l HCl and then evaporated to dryness. The sample was finally dissolved in 5 ml of 0.5 mol/l HNO_3 for ICP-MS measurement. The detection of ^{239}Pu, ^{240}Pu and ^{242}Pu was performed with X Series^{II} ICP-MS instrument under hot plasma conditions. The details for the ICP-MS instrumentation can be found elsewhere (Qiao *et al*. 2011 a, b)

2.1.2 DTU-Pu-II method

The schematic procedure for Pu determination using DTU-Pu-II method is illustrated in Figure 1. The sample was ashed and acid digested following the sample protocol as described in DTU-Pu-I method. After adding 2.5 mol/l $NH_3 \cdot H_2O$ to pH 8-9 to perform the first iron hydroxide co-precipitation, 30 ml of 6 mol/l NaOH was added to the residue to dissolve amphoteric elements and the sample was centrifuged again. After reducing Pu to Pu(III) with $K_2S_2O_5$ as described in DTU-Pu-I method, the precipitate was dissolved with 5 ml of 14 mol/l HNO_3. The sample solution was finally diluted to 1 mol/l HNO_3 with 0.1 mol/l HNO_3, and 100 mg of $NaNO_2$ was added to oxidize Pu(III) to Pu(IV) (Qiao *et al*. 2009).

A multi-sample processing sequential injection (SI) system was used for the chromatographic purification of Pu, wherein nine samples can be handled sequentially (see Figure. 2). The SI system was detailed elsewhere (Qiao *et al*. 2011 a, b). Nine of 2-ml columns (0.5 cm i. d. × 10 cm length) packed with TEVA resin (100-150 µm particle size)

were integrated in the system, whereupon the chemical purification was controlled automatically via FIAlab software. The chromatographic purification of Pu consists the following steps: 1) Rinse the holding coil with 20 ml of 1 mol/l HNO_3 at flow rate of 5 mL/min. 2) Precondition the column with 20 ml 1 mol/l HNO_3 at 3 mL/min. 3) Load the sample solution onto the column at 1 mL/min. 4) Rinse the column with 60 ml of 1 mol/l HNO_3, followed by 60 ml of 9 mol/l HCl at 2.5 mL/min. 5) Elute Pu with 20 ml of 0.1 $NH_2OH{\cdot}HCl$ in 2 mol/l HCl solution. Pu eluate was evaporated to dryness on a hotplate with the addition of few millilitres of 14 mol/l HNO_3 to decompose the remaining $NH_2OH{\cdot}HCl$. The sample was finally dissolved in 5 ml 0.5 mol/l HNO_3 for ICP-MS measurement as described in DTU-Pu-I method.

2.2.3 UH-Pu-I method

10 g of soil sample was dried at 105 °C. 50 mBq of ^{242}Pu tracer (and 30 mg of Sr carrier for ^{90}Sr determination) were added to the sample. The sample was heated to boiling and digested with 100 ml of 14 mol/l HNO_3 on a hot plate for 6 h. H_2O_2 was added dropwise (1-2 ml per sample) 1 h before ending the digestion. After cooling, the sample was filtered through a GF filter and the filtrate was evaporated to dryness.

The residue was dissolved with 80 ml of 8 mol/l HNO_3 with heat. Solid $NaNO_2$ was added to a warm solution for stabilizing Pu as Pu(IV). The solution was further heated for 30 min., and then cooled for about 1 h. Sample solution was loaded to an 8-mL column packed with Dowex 1 x 4 (50-100 mesh) anion exchange resin preconditioned with 30 ml of 8 mol/l HNO_3. The column was washed with 50 ml of 8 mol/l HNO_3. The effluent from sample loading and 8 mol/l HNO_3 washing were collected for further purification of Sr. The column was washed with 12 mol/l HCl to remove thorium. Finally, Pu was eluted with the mixture of 60 ml of 12 mol/l HCl and 8 ml of 1 mol/l NH_4I. The schematic procedure for Pu chromatographic separation is illustrated in Figure 3.

Pu eluate obtained above was further purified with UTEVA+TRU extraction chromatographic columns as indicated in Figure 4. In detail, the Pu eluate was evaporated to dryness and the residue was dissolved with 20 ml of 3 mol/l HNO_3 + 1 mol/l $Al(NO_3)_3$ solution. 2 ml of 0.6 mol/l ferrous sulphamate solution and 150 mg of ascorbic acid were added to reduce and stabilize Pu as Pu(III). After 15 min, the sample was loaded to a 2-mL UTEVA column which was then washed with 10 ml of 3 mol/l HNO_3. Both effluents from UTEVA column were collected and then directly loaded to a 2-ml TRU column. Pu was eluted with 10 ml of 4 mol/l HCl + 0.02 mol/l $TiCl_3$. 50 µg of Nd carrier and 1 ml of 23 mol/l HF were added to Pu eluate to co-precipitate Pu with NdF_3. The precipitate was filtered to a 0.1 µm filter. Activities of ^{238}Pu and $^{239+240}$Pu were measured by alpha spectrometer (Alpha Analyst, Canberra) for 7 days.

2.2.4 UH-Pu-II method

10 g of soil was ashed in a muffle furnace at 450 ˚C overnight. ^{242}Pu-tracer was added for chemical yield determination. The sample pretreatment was performed according to the same procedure in UH-Pu-I method. After evaporating the filtrate to dryness, the sample was dissolved with 20 ml of 3 mol/l HNO_3 + 1 mol/l $Al(NO_3)_3$ solution. Pu was then reduced to Pu(III), purified with UTEVA-TRU extraction chromatographic columns and then measured with alpha spectrometry following the same protocol described in UH-Pu-I method.

2.2.5 IFE-Pu-I method

10 g of soil was dried under 105°C overnight and then ashed at 450°C overnight. The sample was spiked with about 18 mBq of ^{242}Pu as a chemical yield tracer for Pu (and also about 5 Bq of ^{85}Sr tracer for ^{90}Sr determination). The sample was digested with 100 ml of *Aqua regia* on a hotplate at 120°C for 7 h with the addition of H_2O_2. After evaporation to dryness, 28 mol/l HF and 14 mol/l HNO_3 were added, and the sample was evaporated to dryness again. 1.0 g of NH_2OH HCl and 100 mg of Ca carrier were added. The sample was dissolved with 1 mol/l HNO_3, and 10 g of oxalic acid was added. $NH_3 \cdot H_2O$ was added to pH 5-6 and the sample was heated for 1 h at 110 °C. After cooling, the sample was filtered through a Whatman 42 grade filter. The beaker and the filter paper were washed with 30 ml of 0.8 mol/l oxalic acid solution. The precipitate on the filter was dried under 110 °C for 15 h, and then ashed under 450 ° C for 5 h and 600 °C for 17h , respectively.

The ashes were dissolved with 5 ml of 14 mol/l HNO_3 and then evaporated to dryness. The sample was finally dissolved in 20 ml 3 mol/l HNO_3 – 0.1 mol/l sulfamic acid – 0.1 mol/l ascorbic acid and loaded onto a tandem UTEVA-TRU-Sr cartridge (2-mL volume of each column, 100-150 µm particle size). The tandem set-up of columns was washed with 10 ml of 3 mol/l HNO_3 and thereafter the three columns were split. The TRU column was washed with 10 ml of freshly prepared 3 mol/l HNO_3 – 0.1 mol/l $NaNO_2$ followed by 2 ml of 9 mol/l HCl and 20 ml of 4 mol/l HCl. Pu was eluted from TRU with 10 ml 4 mol/l HCl + 0.2 ml 15 % $TiCl_3$ in a 20 ml scintillation vial. 100 µL Ce(III) solution (500 µg Ce/mL) and 2 ml of 28 mol/l HF were added to the Pu eluate and allowed to sit for 30 min. The precipitate was filtered through a Resolve® filter. Activities of ^{238}Pu and $^{239+240}$Pu were measured by an Ortec alpha detector for 9 days.

2.3 Determination of ^{90}Sr in soil

2.3.1 DTU-Sr-I method

10 g of soil was ashed at 550 °C overnight. After the addition of ^{85}Sr (5-10 Bq) as a chemical yield tracer and 0.5 g of $SrCl_2 \cdot 6\ H_2O$ as carrier, 320 ml of aqua regia was added. The sample was digested at 150 ^{0}C on hotplate for 2 h. After cooling, the sample was filtered with a GF/A filter and the residue was washed with 300 ml of 0.2 mol/l HCl. The solution was evaporated to 100 ml and 6 mol/l NaOH was added to pH 6 to form $Fe(OH)_3$ precipitate. After centrifugation, the supernatant was collected in a beaker. 10 ml of 12 mol/l HCl was added to dissolve the precipitate and the $Fe(OH)_3$ precipitation was repeated until ^{85}Sr activity in the precipitate is less than 3% of the total ^{85}Sr activity spiked.

All the supernatants obtained were combined and 200 ml of 6 mol/l NaOH was added to form $Ca(OH)_2$ precipitate. The supernatant after centrifugation was heated to boil and Na_2CO_3 (5 g Na_2CO_3 per100 ml solution) was added to form $SrCO_3$ precipitate. The sample was heated on a hot plate at 250-300 ^{o}C for 1 h. After cooling, the sample was centrifuged and the supernatant was discarded. 4 ml of 8 mol/l HNO_3 was added to dissolve the $SrCO_3$ precipitate. NaOH was added to pH 10 and 10 ml of 6 mol/l NaOH was added to form $Ca(OH)_2$ precipitate. After centrifugation, the supernatant was collected and heated to boil. 10 g of Na_2CO_3 was added and the sample was heated at 220 ^{o}C for 1 h. $Sr(NO_3)_2$ precipitation was performed twice with the addition of 14 mol/l HNO_3. The $Sr(NO_3)_2$ precipitate was dissolved with 50 mL ultrapure H_2O and 5 mg of Fe (as $FeCl_3$) was added. NaOH was added to pH 10. After centrifugation, 7.5 mg of Y carrier (as YCl_3), 10 mg of Ba carrier (as $BaCl_2$)

and 1 ml of 12 mol/l HCl were added to the supernatant. ^{85}Sr was measured by NaI gamma detector for determining the chemical yield of ^{90}Sr until the current step and the sample was left to stand for three weeks to allow the ingrowth of ^{90}Y.

After three weeks, 6 mol/l NH_3 was added to the sample to pH >10 to form $Y(OH)_3$ precipitate. After centrifugation, 1 ml of 6 mol/l HNO_3 was added dissolve the $Y(OH)_3$ precipitate, and 5 mg Sr carrier (as $SrCl_2$) was added. The $Y(OH)_3$ precipitation was repeated once. 1 ml of 6 mol/l HNO_3 was added to dissolve the $Y(OH)_3$ precipitate. 5 mg of Ba^{2+}carrier and 2 mg of Sr^{2+} carrier were added. $BaSO_4$ and $SrSO_4$ precipitation was formed with the addition of 1 ml of 2 mol/l H_2SO_4. After centrifugation, the $BaSO_4$ and $SrSO_4$ precipitate was discarded. 6 mol/l NH_3 was added to the supernatant to pH >10 to form the $Y(OH)_3$ precipitate.

The $BaSO_4$ and $SrSO_4$ precipitation were repeated twice. 25% NH_3 was added to the supernatant to pH >10 to form the $Y(OH)_3$ precipitate. Thereafter five drops of 6 mol/l HNO_3 was added to dissolve the sample. 20 ml of 0.8 mol/l $H_2C_2O_4$ was added to form $Y_2(C_2O_4)_3$. The $Y_2(C_2O_4)_3$ precipitate was filtered and delivered to β-measurement by a low background gas flow Geiger Müller (GM) beta counter (Risø beta counter, Denmark). Stable yttrium is used to monitor the chemical yield of ^{90}Y in the Sr-Y separation step and quantified by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.3.2 UH-Sr-I method

10 g of soil was pre-treated according to the procedure described in UH-Pu-I method. The effluent collected for Sr purification from the anion exchange (Dowex 1 x 4) chromatography was evaporated to dryness and the residue was re-dissolved in 50 ml of 8 mol/l HNO_3. The sample was loaded to a preconditioned 8-mL Sr resin®. After washing with 20 ml of 8 mol/l HNO_3, 10 ml of 3 mol/l HNO_3 + 0.05 mol/l $H_2C_2O_4$ and 10 ml of 8 mol/l HNO_3, respectively, Sr was eluted with 50 ml of 0.05 HNO_3. The schematic procedure is illustrated in Figure 5.

Sr was precipitated as $SrCO_3$ after adding 1 g of $NH_2CO_2NH_4$. The chemical yield of Sr was determined gravimetrically. The precipitate was filtered through a membrane filter (Millipore 0.45 µm). The precipitate was dried and transferred to a liquid scintillation vial and 2 ml of 4 mol/l HCl and 18 ml of H_2O was added. After 3 weeks in-growth of ^{90}Y, the activity of ^{90}Sr was determined with Quantulus 1220 liquid scintillation counter in a Cerenkov counting mode for 10 h.

2.3.3 FOI-Sr-I method

1 g of soil sample was added to a graphite crucible. After the addition of 1 mg stable Sr as a chemical yield tracer and about 4 g $LiBO_2$ as fusion flux, the sample was pre-oxidized in a muffle furnace at 650 °C for 1 h. After pre-oxidation, the sample was melted at 1050 °C for 15 min, or until the sample was completely melted. After cooling, the sample was dissolved in 100 ml of 1.4 mol/l HNO_3 while being stirred and heated. PEG2000 was added to flocculate Si in solution to avoid clogging during the solid phase extraction chromatograph. The sample was evaporated to 50 mL and then filtered with a Millipore OOM filter paper. To the filtrate, 14 mol/l HNO_3 was added to achieve a final concentration of 8 mol/l HNO_3. 0.1 ml of aliquot was taken for stable Sr analysis by ICP-OES.

The chromatographic purification of Sr was performed with a vacuum box, where 2-mL Sr-resin cartridge was mounted on the top. After preconditioning the cartridge with 10 ml of 8 mol/l HNO_3, the sample solution was loaded onto the column. The column was rinsed with 10 ml of 8 mol/l HNO_3, 10 ml of 3 mol/l HNO_3-0.05 mol/l $H_2C_2O_4$ and 10 ml of 8 mol/l HNO_3, respectively. Strontium was then eluted using 15 ml of 0.05 mol/l HNO_3. 0.1 ml of aliquot was taken for stable Sr analysis by ICP-OES (iCap 7000) to determine the chemical yield of Sr. In order to avoid interferences from the ingrowth of ^{90}Y from ^{90}Sr, an immediate 15 min Cherenkov counting of ^{89}Sr is performed. After allowing about 16 h of in-growth, the sample was measured for its ^{90}Y activity by Cherenkov counting on a Quantulus 1220 liquid scintillation counter for 4 h.

2.3.4 IFE-Sr-I method

10 g of soil was pre-treated according to the procedure described in IFE-Pu-I method. After splitting the Sr column from the UTEVA and TRU resin, the Sr column was washed with 10 ml of 8 mol/l HNO_3 followed by 5 ml of 3 mol/l HNO_3 – 0.05 mol/l oxalic acid and 5 ml of 3 mol/l HNO_3, respectively. Sr was eluted with 10 ml of 0.05 mol/l HNO_3 in a 20 ml scintillation vial. The activity of ^{85}Sr was detected by NaI gamma detector to calculate the chemical yield of ^{90}Sr in the previous process. 10 mg of Y carrier (as YCl_3) was added.

After 14 days in-growth of ^{90}Y, 12 mol/l HCl was added to the sample to pH 2. The sample was heated to 90 °C and 6 mol/l $NH_3 \cdot H_2O$ was added to pH 8 to form $Fe(OH)_3$-$Y(OH)_3$ precipitate. After addition of 6 drops of H_2O_2, the sample was kept at 90 °C for 1 h. After cooling and centrifugation, the precipitate was dissolved with 3-4 drops of 12 mol/l HCl and 15 ml of deionized water. The sample was heated to 90 °C again and the $Fe(OH)_3$-$Y(OH)_3$ precipitation was repeated twice. The precipitate was dissolved with 3-4 drops of 12 mol/l. HCl and 15 ml of deionized water. 6 mol/l $NH_3 \cdot H_2O$ was added to adjust pH to 2. After addition of 20 mg of Pb carrier (as $PbCl_2$), 2 ml of saturated $NaSO_4$ was added. The precipitate was filtered through a 0.45 µm membrane filter and the filtrate was heated to 90 °C. 1 ml of saturated oxalic acid solution was added dropwise and then 6 mol/l $NH_3 \cdot H_2O$ was added to pH 2-3. The sample was kept at 90 °C for 1 h. The $Y_2(C_2O_4)_3$ precipitate was filtered through a GF/A filter and then measured with a low background GM beta counter (Risø beta counter, Denmark).

After the beta counting, the filter was combusted at 900 °C for 1.5 h and the remaining Y_2O_3 was dissolved with 3 ml of 14 mol/l HNO_3. The sample was evaporated to dryness and then dissolved in 20 ml acetate buffer solution (pH=4). After adding 1 drop of xylenol orange, the Y concentration was titrated with 0.01 mol/l EDTA.

2.4 Determination of ^{90}Sr in milk

2.4.1 DTU-Sr-II method

100g of dry milk was ashed at 550 ^{0}C in oven for three days. After adding 5-10 Bq ^{85}Sr tracer and 0.5 g $SrCl_2 \cdot 6\ H_2O$, and 40 ml aqua regia, the sample was digested at 150 ^{0}C for 30 min and 200 ^{o}C for 1 h, respectively. The sample was diluted with ultrapure water to 120 ml and filtered through a GF/A filter paper. 30 ml of 0.8 mol/l $H_2C_2O_4$ was added to the filtrate and 6 mol/l NH_3 was added to pH 7-10. The supernatant was discarded after centrifuge. 30 ml of 14 mol/l HNO_3 was added to dissolve the sample and fuming HNO_3 was added to a concentration of $HNO_3 \geq 14$ mol/l in the solution to precipitate Sr as $Sr(NO_3)_2$. This step was

repeated twice and the residue was dissolved with ultrapure water followed by addition of 5 mg Fe^{3+} (as $FeCl_3$) NaOH was added to pH 10 and the supernatant was separated by centrifugation. 5 mg of Y^{3+} and 1 mg of Ba carrier, 1 ml of 12 mol/l HCl were added to the supernatant. The sample was kept three weeks for the ingrowth of ^{90}Y. After three weeks, ^{90}Y was separated and measured following the same procedure described in DTU-Sr-I method.

2.4.2 UH-Sr-II method

50 g of milk powder was ashed in a muffle furnace in 450 ˚C overnight. The ash (ca. 7-8 g) was dissolved with 50 ml of 8 mol/l HNO_3 and 30 mg of Sr carrier ($SrCl_2$) was added to the samples for determining the chemical yield of Sr. The sample was heated to enhance dissolution of ash. After cooling, the sample solution was loaded to an 8-mL preconditioned Sr resin column. The separation of Sr was performed according to Figure 5.

Sr was precipitated as $SrCO_3$ after adding 1 g of $NH_2CO_2NH_4$. The chemical yield of Sr was determined gravimetrically. The precipitate was filtered through a membrane filter (Millipore 0.45 µm) and the filter was weighed before and after filtration. The precipitate was dried and transferred to a liquid scintillation vial and 2 ml of 4 mol/l HCl and 18 ml of H_2O was added.

2.4.3 FOI-Sr-II method

0.5 g of milk powder (no prior ashing) was added to a Teflon vessel along with 10 ml 14 mol/l HNO_3. Stable strontium (1 mg) was added to the sample for yield determination purposes. The sample was left to pre-digest for 10 min. The vessel was closed and the sample was digested in a Mars5 microwave for approximately 30 min. After cooling, any remaining organic matter was dissolved by adding 30% hydrogen peroxide. Following a filtration, with Millipore OOM filter paper, the sample was then diluted to approximately 8 mol/l HNO_3. A 0.1 ml aliquot was taken for yield determination by stable Sr analysis on ICP-OES. The chromatographic separation for Sr and the subsequent measurement was performed according to the protocol described in FOI-Sr-I method.

2.4.4 IFE-Sr-II method

100 g of milk powder was dried at 105 °C overnight. 20 mg of Sr carrier (as $SrCl_2$), 10 mg of Y carrier (as YCl_3) and 5 Bq of ^{85}Sr spike were added, and the sample was ashed at 500 °C overnight. The ash was dissolved with 50 ml of 14 mol/l HNO_3. The sample was transferred to a separation funnel and 50 ml of TBP was added. After shaking for 5 min., the organic and aqueous phases were separated and the aqueous fraction was discarded. The TBP extraction was repeated for one more time and the date and time was recorded. The organic phase was washed with deionized water and the washes was then evaporated to dryness. The sample was heated to 90 °C and 6 mol/l $NH_3 \cdot H_2O$ was added to pH 8. The sample was centrifuged and the residue was dissolved with 2 drops of conc. HCl and 15 ml of deionized water. The sample was heated to 90 °C again and 1 ml of saturated oxalic acid solution was added drop by drop. 25% $NH_3 \cdot H_2O$ was added to pH 2-3. The sample was kept at 90 °C for 1 h. The $Y_2(C_2O_4)_3$ precipitate was filtered through a GF/A filter and then measured with GM beta counter (Risø beta counter, Denmark). After the beta counting, the Y concentration was titrated with 0.01 mol/l EDTA as described in IFE-Sr-I method.

3 Results and discussion

3.1 Inter-comparison results for Pu in soil

3.1.1 Overview of analytical methods for Pu in the inter-comparison

As indicated in the Material and Methods section, five analytical methods were used for Pu determination in the inter-comparison exercise. For the sample pre-treatment, acid digestion was applied in all five methods. Aqua regia was used in DTU-Pu-I, DTU-Pu-II. HNO_3 was used in UH-Pu-I and UH-Pu-II method with the assistance of H_2O_2 to decompose organic matters contained in the samples. HF and H_2O_2 were used in combination with aqua regia in IFE-Pu-I method to enhance the dissolution of the sample and decompose organic matters. However, it was observed that in IFE-Pu-I method, the soil samples were still difficult to dissolve and despite the use of HF, it was not possible to fully dissolve the Syrian soil. FOI did not take part in the plutonium inter-comparison, thus their method has not been presented in this work. However, in FOI's method for plutonium in soil lithium metaborate fusion is used, which completely dissolves refractory oxides (Nygren *et al*.,2003)

After acid digestion, co-precipitation was used in DTU-Pu-I and DTU-Pu-II methods for a preliminary elimination of matrix elements, while a direct evaporation was performed in UH-Pu-I, UH-Pu-II and IFE-Pu-I methods. For the chemical purification of Pu after the pre-treatment, either anion exchange or extraction chromatography or their combination was used. For example, a single anion exchange column (AG 1x4) was used in DTU-Pu-I method, while a single TEVA column was used in DTU-Pu-II method. UTEVA/TRU tandem column was employed for UH-Pu-I, UH-Pu-II and IFE-Pu-I methods. An automated sequential injection (SI) system was used for the TEVA column separation in DTU-Pu-I method, and a vacuum box system was used for the UTEVA/TRU column separation in IFE-Pu-I method. Manual fashion was performed in the chromatographic separation in the other three methods. Among the five analytical method used for Pu detection, ICP-MS measurement was used in DTU-Pu-I and DTU-Pu-II methods, while traditional alpha spectrometry was used in the other methods.

In the analysis for Syrian soil using UH-Pu-I method, due to the high matrix content in the sample, it was not possible to use extraction chromatography directly, therefore an ion exchange chromatographic separation was performed firstly. Four blank samples were analysed for Pu to evaluate possible cross-contamination between the samples and no cross-contamination was found. Since the matrix content in Danish soil was low, the residue after wet-ashing and evaporation in the UH-Pu-II method was quite small, therefore, it was possible to use only extraction chromatography step for separating Pu.

3.1.2 Accuracy and precision of each method

The overall results for Pu determination in the inter-comparison exercise are summarized in Table 2. Two tests were used to evaluate the results obtained: the relative bias test and the precision test.

The relative bias is calculated as $Bias = \frac{V_i - V_r}{V_r} \times 100\%$

Where *Bias* is the relative bias of each analysis, *Vi* is the value obtained by each method in the inter-comparison exercise, *Vr* is the reference value of the corresponding samples.

The precision was calculated as $P = \sqrt{(\frac{u_r}{V_r})^2 + (\frac{u_i}{V_i})^2} \times 100\%$

Where P is the precision of each analysis, Vi and u_i is the value and uncertainty obtained by each method in the inter-comparison exercise, Vr and u_r is the reference value of the corresponding samples.

The criterias for accuracy and precision tests are according to IAEA recommendation (I. Osvath *et al.* 2016). If the Bias < MARB (Maxiumum Acceptable Relative Bias) the result will be "Acceptable" for accuracy. And if Bias < k*P (k=2.56) and P< MARB then the result will be acceptable for "precision" as well. MARB for Pu analysis is set to be 25%.

The reference value of $^{239+240}$Pu in the Syrian soil (IAEA-TEL-2015 no.5) is 2.7 ± 0.4 Bq/kg. The results obtained using DTU-Pu-I and UH-Pu-I methods are 2.82 ± 0.07 Bq/kg and 2.50 ± 0.10 Bq/kg, respectively, which agree well the reference value with relative bias < 8%. For the Danish soil, the recommended value of $^{239+240}$Pu is 0.238 ± 0.014 Bq/kg, with 0.140 ± 0.014 Bq/kg of ^{239}Pu and 0.098 ± 0.01 Bq/kg of ^{240}Pu of, respectively. The results reported for thetwo methods used (DTU-Pu-II and IFE-Pu-I) agreed with the reference value. $^{239+249}$Pu concentration obtained using UH-Pu-II method indicates -16% relative bias, while the other two results by using DTU-Pu-II and IFE-Pu-I methods show relative bias within 5%. The P values (about 15%) obtained in DTU-Pu-I and UH-Pu-I method are comparable, and range from 12 % to 25% in the Pu results for Danish soil using DTU-Pu-II, UH-Pu-II and IFE-Pu-I method. The overall results obtained in this inter-comparison for Pu determination passed both relative bias test and precision test, indicating satisfactory accuracy and precision for the reported methods.

For the pre-treatment of environmental solid samples, acid digestion using mineral acid (e.g., HNO_3, HCl or aqua regia) is a simple and straightforward method, which is commonly used for the determination of Pu. With the increase of aggressiveness of acid, the extraction efficiency of Pu would be increased. This might be a possible explanation for the somewhat low results obtained by using UH-Pu-I and UH-Pu-II methods. Since only 14 mol/l HNO_3 was used for acid digestion in both methods. Acid digestion may result in incomplete extraction of Pu, leading to that the tracer added may be extracted fully, whilst plutonium within the sample is partially extracted, thereby resulting in low activity levels despite correction for chemical yield.

It should also be noted that acid digestion without total dissolution might not be suitable for samples containing refractory Pu oxides, since Pu refractory oxides may hardly be extracted by acid leaching. Nevertheless, since the two soil samples analysed in this inter-comparison exercise are environmental samples with Pu origin from global fallout, therefore, the content of Pu refractory oxides in these two samples is negligible. Consequently, application of acid digestion (with e.g., aqua regia) in the treatment should be able to obtain reliable results for Pu. However, work done by Nygren *et al.* (2003) has shown that in some sediment reference materials there may be refractory Pu oxides, indicating that it is of importance to choose a sample digestion method that completely dissolves the sample.

In the chromatographic purification process, TEVA indicates higher absorption capacity for Pu(IV) and superior decontamination of U compared to traditional anion exchange resin. However, experiences have shown that TEVA is sometimes more sensitive to matrix content in the sample solution compared to anion exchange resin (Xu et al. 2013). In cases of

handling complex matrices or high matrix content samples, a guard column (normally anion exchange column) is needed to avoid the breakthrough or deteriorated performance of the TEVA column. In the experiment, it was observed that Syrian soil is very fine-grained and contains iron-rich matrix, which is difficult to handle. Therefore, a larger anion exchange column was used in DTU-Pu-I method for the chemical purification of Pu. However, the results indicated that U was not sufficiently removed by using a single anion exchange column separation, in which case an additional calibration was performed to deduct the contribution of $^{238}U^{1}H^{+}$ to ^{239}Pu signal when processing the ICP-MS analysis data. To overcome the high susceptibility of extraction chromatographic resin (e.g., TEVA) to matrix content, development of an alternative co-precipitation technique (e.g., CaC_2O_4) could be considered to eliminate the scavenge of most metal elements (Fe, Mn, Ni, Co) as well as U contained in the samples. As a consequence, one TEVA column separation might be sufficient to purify Pu and thus the analytical time will be reduced comparing to the one using an extra anion exchange column before the TEVA column separation.

It is also noted that relatively low chemical yields (35-45%) of Pu were achieved in UH-Pu-I and UH-Pu-II methods, and the analysis was failed using IFE-Pu-I method. Since no co-precipitation was performed prior to the extraction chromatography in all these three methods, one potential reason for explaining low Pu chemical yields or failure of analysis could be the high competitive adsorption of matrix elements on UTEVA/TRU column separation, or it may be due to losses of Pu(IV), which become retained on UTEVA in the matrix consisting of 3 mol/l HNO_3. Possible improvements of the method would be to perform a preliminary separation using e.g., co-precipitation to diminish the matrix effect on the column separation, or to ascertain that plutonium exists as Pu(III) prior to separation on TRU. Another reason for results not agreeing well with the reference value of a reference material could be that the measurement uncertainty is underestimated. To avoid questions arising regarding measurement uncertainty, budgets should always be available when comparing results.

3.1.3 Analytical turnover time

The entire analytical turnover time for Pu determination is about 1 day for DTU-Pu-I and DTU-Pu-II methods, about 9 days for UH-Pu-I and UH-Pu-II methods and about 13 days in IFE-Pu-I method. Based on the detailed procedures (Appendix I-V) it can be seen that sample ashing, evaporation and alpha spectrometric measurement of Pu are the most time-consuming phases. In emergency cases, the turnover times could be further minimized by shortening the ashing time to few hours, performing co-precipitation instead of evaporation and using ICP-MS instead of alpha spectrometry. In case of alpha spectrometry used (for ^{238}Pu measurement or whenever ICP-MS is not available for ^{239}Pu and ^{240}Pu), source preparation by fluoride co-precipitation (Hindman, 1986) would be faster than electrodeposition method and shorten the source preparation from several hours to 1.5 hours.

Batch-wise sample pretreatment is advantageous to improve the sample throughput, vacuum box and automated chromatographic separation in sequential injection system could ensure the constant analytical speed in the chromatographic separation, since in many cases, the column separation for Pu can be extremely prolonged due to the blockage of column by inseparable particulate matter contained in the sample solution. One advantage of applying a fully automated SI chromatographic separation is to reduce the labour intensity and human errors in the operation. Rapid method is preferable in most analytical works, however, selection of separation and detection methods should also depend on other criteria such as

simplicity of the method, availability of equipment resources, and precision/accuracy required for the analysis.

3.1.4 Detection limit

Different equations were used to calculate the limit of detection (LOD) for ICP-MS and alpha spectrometry measurement, respectively. For ICP-MS, the equation from Miller and Miller (2000) was used:

$$LOD = x_{blk} + 3 \times s_{blk} \quad (1)$$

where x_{blk} is the average concentration of the background signal, s_{blk} the standard deviation of the background. For alpha spectrometry, Currie's (1968) equation was used based on a 95% confidence interval:

$$LOD = 2.71 + 4.65\sqrt{b} \quad (2)$$

where *b* is the counts of background measured.

It can be seen from Table 2 that, the LODs for ^{239}Pu and ^{240}Pu when using ICP-MS measurement (DTU-Pu-I and DTU-Pu-II methods) is 0.00025 and 0.00079 Bq/kg, respectively, which is 2-10 times lower than the values obtained in the methods using traditional alpha spectrometry (0.018, 0.022 and 0.07 Bq/kg of $^{239+240}$Pu in UH-Pu-I, UH-Pu-II and IFE-Pu-I method, respectively). Besides the relatively fast measurement by ICP-MS, another advantage of using ICP-MS is to be able to distinguish between ^{239}Pu and ^{240}Pu, and thereby the isotopic ratio ^{240}Pu/^{239}Pu can be obtained for investigating source terms and other tracer studies. However, it should be noted that alpha spectrometry is so far the only method of choice for the measurement of ^{238}Pu and LODs of 0.012, 0.014 and 0.07 Bq/kg for ^{238}Pu were achieved in UH-Pu-I, UH-Pu-II and IFE-Pu-I method, respectively.

3.2 Inter-comparison result for ^{90}Sr

3.2.1 Overview of analytical methods for Sr in the inter-comparison

Eight different methods have been used for determination of ^{90}Sr in soil or milk in this inter-comparison exercise and the overview of these methods are summarized in Table 3 together with the analytical results for ^{90}Sr. As sample pretreatment all methods employed acid digestion treatment, apart from FOI-Sr-I method which used alkaline fusion. Microwave assisted acid digestion was used in FOI-Sr-II method for processing milk sample. Both alkaline fusion and microwave assisted acid digestion are favorable for the development of rapid radiochemical methods, especially for small sample sizes (e.g., < 10 g). For chemical separation, Sr resin was widely applied in almost all methods. However, some laboratories used a series of precipitation (DTU-Sr-I and DTU-Sr-II) or a TBP extraction (IFE-Pu-II). All methods calculated the concentration of ^{90}Sr by measuring the activity of ^{90}Y by either low background beta counting (DTU-Sr-I, IFE-Sr-I, DTU-Sr-II and IFE-Sr-II methods) or liquid scintillation counting (LSC) (UH-Sr-I, FOI-Sr-I, UH-Sr-II, and FOI-Sr-II methods). For the methods using beta counting, ^{90}Y as $Y_2(C_2O_4)_3$ was separated from ^{90}Sr after a series of precipitations and/or co-precipitations. For separation of ^{90}Y from Sr, Ln-resin has been used by most of the methods, it was also previously used at FOI. However, this method was found to give unfavorable yield of Y (approx. 50-60%) compared to what could be achieved by

using only strontium separation chemistry. Sr-resin has been proved to successfully isolate ^{90}Y with high chemical yields after the ingrowth of ^{90}Sr from ^{90}Y (Holmgren *et al* 2014). For methods involving LSC, no ^{90}Sr-^{90}Y separation was needed since Cerenkov counting, a method that discriminates in favor of high energy beta, was performed for ^{90}Y after in-growth. However, this approach is only possible when there is no ^{89}Sr present in the sample. By measuring Cherenkov counting directly after isolation of Sr, i.e. assuring that no ^{90}Y has started to grow in, one can make sure that there is no ^{89}Sr present in the sample.

One way of determining the yield is to add stable Sr as a chemical yield tracer (UH-Sr-I, FOI-Sr-I/II, and UH-Sr-II) and determining it gravimetrically (UH-Sr-I and UH-Sr-II methods) or by ICP-OES (FOI-Sr-I/II method). Another way, as used by the other four methods, is to use ^{85}Sr as a radioactive yield tracer, measured by gamma spectrometry to determine the chemical yield of Sr. It was observed in gravimetric determination of Sr that handling and weighing of the $SrCO_3$ precipitation was not as easy or convenient as it was to measure Sr-concentration directly from the 0.05 HNO_3 eluate after Sr-separation, by e.g. ICP-OES. The repeatability of gravimetrical measurement of Y is not very good due to the low stability of the weighing device. Determination of Y chemical yield was needed whenever Y-Sr separation was performed before beta counting in DTU-Sr-I, IFE-Sr-I, DTU-Sr-II and IFE-Sr-II methods. Stable Y (^{89}Y) was used in all methods during the Sr-Y chemical separation and was measured either by EDTA titration (IFE-Sr-I and IFE-Sr-II methods) or by ICP-OES (DTU-Sr-I and DTU-Sr-II methods).

3.2.2 Accuracy and precision of each method

Both relative bias test and precision test were used to evaluate the analytical results obtained for ^{90}Sr determination in the inter-comparison exercise. Same equations as described in the discussion for Pu results were used to calculation of relative bias (Bias) and precision (P) for ^{90}Sr. The criterias for accuracy and precision tests are also according to IAEA recommendation (I. Osvath *et al.* 2016) as mentioned before. MARB for Sr analysis is set to be 25%.

The reference value of ^{90}Sr in Syrian soil (IAEA-TEL no.5) is 36.2 ± 2.7 Bq/kg. The ^{90}Sr concentrations obtained using DTU-Sr-I, IFE-Sr-I and FOI-Sr-I methods were 34.2 ± 4.7, 39.0 ± 3.0 and 42.3 ± 7.3 Bq/kg, respectively. These results show satisfactory accuracy, given a Maximum Acceptable Relative Bias of 20%, with calculated relative bias of -5.5%, 7.7% and 16.8%, respectively. However, the ^{90}Sr value for Syrian soil obtained by the UH-Sr-I method significantly differs from the reference value with relative bias of -60.6%. The detailed reason for such large deviation has been evaluated by the laboratory in question, which might be related to the low repeatability of gravimetrical measurement of Y, unknown quenching effect in the LSC measurement caused by the color of the $SrCO_3$-precipitates (Figure 6) and/or incomplete leaching of ^{90}Sr using 14 mol/l HNO_3. To reduce the uncertainty in the Sr chemical yield monitoring, alternative method using either ICP-OES, AAS or ion chromatography should be therefore preferred (Salminen and Paatero 2009, Salminen-Paatero and Paatero 2012). Performing a thorough uncertainty analysis giving an uncertainty budget (by using the software GUM workbench) might be helpful in evaluating which parameter among the ones mentioned above that could be the key contributor to such large variation in the results (Vesterlund *et al.* 2009). As indicated in Table 3, except UH-Sr-I method, P values obtained by the other three methods for Syrian soil are within 20%, indicating these three methods also passed the defined precision test.

The milk powder (DM-1) used in this inter-comparison exercise is one of routine-based samples within Danish monitoring programme, and expected to have ^{90}Sr concentration comparable to the typical Danish milk. The three results of 0.131 ± 0.016, 0.118 ± 0.009, 0.188 ± 0.026 Bq/kg obtained by DTU-Sr-II, UH-Sr-II and IFE-Sr-II method, respectively, with an average value of 0.146 ± 0.037 Bq/kg, are comparable to the ^{90}Sr concentration in typical Danish milk. When using the average of these three values as a reference value for DM-1, the relative bias obtained for the result in DTU-Sr-II, UH-Sr-II and IFE-Sr-II method is -10.1%, -19.0% and 29.1%, respectively. However, due to the relatively high standard deviation (RSD=25.3%) calculated from the three results, P values obtained for all three methods are in the range of 25-30%. Due to the lack of 'true' reference value, conclusion cannot be given herein regarding the performance of each method in relative bias and precision tests. The relative Bias and P values presented in Table 3 are for reference only. This is also a lesson learned from this project that a confident reference value is very important in an inter-comparison exercise in order to evaluate the individual result reported by each method. For cases where no reference value is available it will be difficult to draw conclusions regarding the methods used in the intercomparison.

3.2.3 Analytical turnover time and sample throughput

The turnover time for ^{90}Sr determination in Syrian soil is about 30.3, 23.5, 22.5 and 1.8 days in DTU-Sr-I, UH-Sr-I, IFE-Sr-I and FOI-Sr-I method, respectively. The turnover time for ^{90}Sr determination in Danish milk is about 32.0, 23.5, 11.5 and 1.0 day in DTU-Sr-II, UH-Sr-II, IFE-Sr-II and FOI-Sr-II method, respectively. The sample pretreatment (1-3 days), ^{90}Y ingrowth (16 h to 3 weeks) and LSC/beta counting (4 h to 7 days) are the major time consuming stage in these methods. In the sample pretreatment, optimizations can be carried out to reduce the total analysis time. This can be done e.g. by testing microwave digestion instead of leaching for soil samples, or wet ashing (using a mixture of $HNO_3 – HClO_4 – H_2O_2$ for example) or microwave digestion for milk samples. A 3 week ^{90}Y ingrowth time was used in both DTU-Sr-I and UH-Sr-I method, 2 week ^{90}Y ingrowth in IFE-Sr-I and 16 h ^{90}Y ingrowth in FOI-Sr-I method.

DTU-Sr-I and DTU-Sr-II methods provide low detection limits and good counting statistics (for 7 days counting). However, the DTU-Sr-I/II analytical procedure is in general tedious and time consuming due to the repeated precipitation or co-precipitation. Also it involves the use of fuming nitric acid, which causes a potential safety risk for the analysts. This leads to relatively low sample throughput, high labour intensity and thus high analytical cost. The IFE-Sr-II method is relatively safe as neither fuming nitric acid nor hydrofluoric acid was used, but it is also somewhat time consuming (Appendix VII) and requires many different chemicals.

The benefits from the thorough chemical purification and low background GM beta counting after the full ingrowth of ^{90}Y are the high decontamination for interfering elements and sufficiently low detection limits. The analytical speed can be prompted via either shortening the ^{90}Y ingrowth time and GM beta counting time, or using LSC measurement for ^{90}Y after a short ingrowth. On the other hand, the detection limit might be increased to some extend which can be investigated in the future work. Moreover, shortening the sample combustion time by increasing the temperature and using Sr extraction chromatographic separation instead of repeated precipitation/co-precipitation could certainly improve the analytical efficiency and method simplicity. It was observed in the UH-Sr-I method that, due to the high content of matrix elements in the sample loading solutions, the column separation

was very slow. In such cases and automated, or vacuum box assisted, column separation might be an advantage to improve the analytical speed.

Both FOI-Sr-I and FOI-Sr-II methods are rapid methods for determining ^{90}Sr, which take less than 48 h to deliver reliable results. Both methods are easy to handle and suitable to samples with varying matrix composition, thus having high applicability. Three batches of 14 samples can be digested within three hours by the Mars5 microwave, and within another six hours, another 42 samples can be digested, taking consideration of acid washing of the sample vessels prior to each digestion. Within 24 hours, 13 batches of 14 samples is the possible sample preparation throughput.

It is also important to note that when ^{89}Sr is present and ^{90}Y has been separated, to determine ^{90}Sr by Cherenkov counting, it is imperative to limit the amount of samples to be measured. This is to ensure that the contribution from the counting uncertainty, for the final sample in a series, does not dominate the total combined uncertainty to an extent where the results risk becoming invalid. This is especially important when dealing with low activity samples where ^{90}Y is separated before full ingrowth, as shown by Tovedal *et al.* (2009 a, b). The FOI-Sr-I/II method is validated for both partial ingrowth as well as full ingrowth. In case there is ^{89}Sr present in the sample then a longer time of ingrowth can be allowed. However, ^{89}Sr activity levels will indicate the activity level of ^{90}Sr since the most demanding ^{89}Sr/^{90}Sr activity ratios are known (Tovedal *et al.* 2009). FOI-Sr-I/II method can be easily adjusted to allow for the most time efficient measurement strategy depending on the ^{89}Sr level.

3.2.4 Limit of Detection

The following equation, as described by Holmgren *et al.* (2016), Lochamy (1976) and Currie (1968), was used to calculate the Limit of Detection (LOD) for ^{90}Sr

$$LOD = \frac{1}{U \cdot m \cdot \Psi} \frac{k^2 + 2k\sqrt{2}\sqrt{R_{BG} t_m}}{\frac{(1 - e^{-\lambda_Y t_m})}{\lambda_Y}(1 - e^{-\lambda_Y t_i})}$$

Where U is the chemical yield, mol/l is mass of sample in kg, Ψ is the measurement efficiency for the measurement of ^{90}Y by LSC or beta counting, k is 1.64 for a 95% confidence interval, R_{BG} is the count rate in cps for the blank, t_m is the measurement time for the samples, t_i is the time of ingrowth for the samples ($t_i = \infty$ for the methods that awaited full ingrowth of ^{90}Y), λ_Y is the decay constant for ^{90}Y.

The LODs of ^{90}Sr vary from 0.2 to 24 Bq/kg among the four methods for soil analysis and 0.017 to 60 Bq/kg (dry) among the other four methods for milk analysis. Relatively high LODs were achieved by FOI-Sr-I and FOI-Sr-II method compared to the other methods reported in this inter-comparison. Nevertheless, the LODs for the FOI-Sr-I and FOI-Sr-II methods are significantly lower than the generic action limit (100 Bq/L) for milk (WHO, 1988).

4. Conclusions and perspectives

Most methods used in the inter-comparison exercise have successfully determined the activity of Pu isotopes and ^{90}Sr in the relevant samples. Among the five analytical methods reported for $^{239, 240}$Pu determination, novel techniques, namely, sequential injection or

vacuum-box-assisted chromatographic separation have been only applied in DTU-Pu-II and IFE-Pu-I method, respectively. Modern automated or vacuum box assisted chromatographic separation methods have higher analytical efficiency and lower labour intensity compared to the traditional methods based on traditional chromatography based on gravity. It is also apparent that advanced detection technique, i.e., ICP-MS as used in DTU-Pu-I/II method, provide advantages of shortening the measurement time from several days to ten minutes, and reducing the detection limit by several times. All the reported Pu methods used traditional acid digestion for sample pre-treatment which is simple and straightforward. However, the application of alkaline fusion might need to be prompted for samples containing Pu refractory oxides (Croudace *et al.* 1998).

Among the eight reported ^{90}Sr determination methods, vacuum box assisted chromatography was applied in FOI-Sr-I/II and IFE-Sr-I/II methods, while effective sample pre-treatment using alkaline and microwave digestion was only applied in FOI-Sr-I/II method. Apart from the FOI-Sr-I/II method, which could complete the analysis within 1-2 days, all the other methods have very long analytical turnover time. This is a consequence of long-term (2-3 weeks) ingrowth of Y as well as the beta counting involved in these methods. Even though Sr resin has been used in most of the methods, application of effective sample digestion protocol, as used in FOI-Sr-I/II method, and optimization of the pre-concentration operation are necessary to improve the analytical efficiency. There was a large variation (0.2 to 24 Bq/kg for soil and 0.02-60 Bq/kg(dry) for milk) in detection limit for ^{90}Sr among the reported methods, indicating different potential applications for each method. For samples with very low levels of activities of Sr, methods developed for nuclear emergency preparedness situations may not be suitable. When handling very low level samples, large sample sizes are needed to meet the criteria of the detection limit for the measurement techniques (Salminen-Paatero and Paatero 2016). Nevertheless, advanced radiochemical techniques are always desirable when improving analytical performance of methods applied to different fields, this is also true for different requirements in detection limit.

This inter-comparison exercise reflects the fact that the application of novel techniques for radiochemical analyses of hard-to-measure radionuclides, e.g., Pu isotopes and ^{90}Sr is very limited among Nordic countries. The existing knowledge and experiences need be to broaden in order to strength the further development of different novel techniques in radiochemical field. There is an apparent need for every analyst to be aware of the advantages of novel techniques for radiochemical assays in order to become more active in driving the long-term development. Moreover, it would be beneficial to review the methods with regards to measurement uncertainty. This could be a prospect for a future collaboration within the Nordic countries, with potential funding from Nordic Nuclear Safety Research.

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Table 1. Sample list for NKS rapid-tech inter-comparison

Samples for ^{90}Sr		
Sample ID	**Type**	**Description**
IAEA-TEL no.5	Soil	Soil collected from Syria
DM-1	Dry milk	Milk collected from Videbæk, Denmark
Samples for ^{238}Pu, ^{239}Pu, ^{240}Pu		
Sample ID	**Type**	**Description**
IAEA-TEL no.5	Soil	Soil collected from Syria
DS-1	Soil	Soil sample collected from Denmark

Table 2. Overall analytical results for Pu isotopes in the inter-comparison exercise, uncertainties are given for *1*σ

Sample ID	**Method**	**Description**	**Turnover time, h**	**Pu chemical yield, %**	**Pu activity, Bq/kg**		**LOD, Bq/kg**	**Bias, %**	**P, %**
					^{238}Pu	$^{239+240}$Pu			
IAEA-TEL no.5	DTU-Pu-I	Dry ashing - aqua regia digestion- $Fe(OH)_3$ co-precipitation-AG 1x 4 chromatography-ICP-MS	28	80.1 ± 8.0	NM	2.82 ± 0.07*	0.00025 (^{239}Pu) 0.00079 (^{240}Pu)	4.4	15.0
	UH-Pu-I	Conc. HNO_3 + H_2O_2 digestion - evaporation-Dowex + UTEVA/TRU chromatography-alpha spectrometry	216	NA[#]	0.084 ± 0.013	2.50 ± 0.10	0.012 (^{238}Pu) 0.018 ($^{239+240}$Pu)	-7.4	15.3
	IFE-Pu-I	Dry ashing - aqua regia/H_2O_2//HF digestion-evaporation - UTEVA/TRU column - alpha spectrometry	303	NA[#]	NM	NM			
	Reference value				-	2.7 ± 0.4			
DS-1	DTU-Pu-II	Dry ashing - aqua regia digestion- $Fe(OH)_3$ co-precipitation-automated TEVA chromatography-ICP-MS	24	95.3 ± 4.7		0.23 ± 0.03 ^{239}Pu: 0.14 ± 0.01 ^{240}Pu: 0.09 ± 0.02	0.00025 (^{239}Pu) 0.00079 (^{240}Pu)	3.4	14.3
	UH-Pu-II	Dry ashing - conc. HNO_3 + H_2O_2 digestion - evaporation -UTEVA/TRU column - alpha spectrometry	209	NA[#]	< LOD	0.20 ± 0.02	0.014 (^{238}Pu) 0.022 ($^{239+240}$Pu)	-16.0	11.6
	IFE-Pu-I	Dry ashing - aqua regia/H_2O_2//HF digestion-evaporation - UTEVA/TRU column - alpha spectrometry	303	25.6 ± 2.6	< LOD	0.25 ± 0.06	0.07 (^{238}Pu) 0.07 ($^{239+240}$Pu)	5.0	24.7
	Reference value					0.238 ± 0.014 ^{239}Pu: 0.140 ± 0.008 ^{240}Pu: 0.098 ± 0.006			

*^{240}Pu:^{239}Pu atomic ratio was measured to be 0.186. [#]NA: not available.

Table 3. Overall analytical results of ^{90}Sr in the inter-comparison exercise, uncertainties are given for *1*σ.

Sample ID	**Method**	**Description**	**Turnover time, h**	**Total chemical yield for Sr analysis, %**	**^{90}Sr activity, Bq/kg***	**LOD, Bq/kg**	**Bias, %**	**P, %**
IAEA-TEL no.5	DTU-Sr-I	Dry ashing - aqua regia digestion - $Fe(OH)_3$ precipitation - repeated $Ca(OH)_2$, $SrCO_3$ and $Sr(NO_3)_2$ precipitation – 3-week ^{90}Y ingrowth- repeated $Fe(OH)_3/Y(OH)_3$ and $BaSO_4/SrSO_4$ precipitation - $Y_2(C_2O_4)_3$ precipitation - beta counting (^{90}Y)	728	70.1 ± 7.0	34.2 ± 4.7	0.4	-5.5	15.6
	UH-Sr-I	Dry ashing - conc.HNO_3/H_2O_2 digestion-evaporation - Dowex 1 x 4+ Sr column – $SrCO_3$ precipitation – 3-week ^{90}Y ingrowth – LSC (^{90}Y Cerenkov counting)	564	41%-79%	14.3 ± 13.1	1.0	60.6	92.2
	IFE-Sr-I	Dry ashing - aqua regia/H_2O_2//HF digestion-evaporation-TUEVA/TRU/Sr column – 2-week ^{90}Y ingrowth- repeated $Fe(OH)_3/Y(OH)_3$ precipitation - $PbSO_4/SrSO_4$ precipitation - $Y_2(C_2O_4)_3$ precipitation - beta counting (^{90}Y)	539	37.0 ± 3.7	39.0 ± 3.0	0.2	7.7	10.7
	FOI-Sr-I	Dry ashing - $LiBiO_2$ fusion - Sr resin – 16 h ^{90}Y ingrowth - LSC (^{90}Y Cerenkov counting)	44	99.5 ± 8.6	42.3 ± 7.3	24	16.8	18.8
	Reference value				36.2 ± 2.7			
DM-1	DTU-Sr-II	Dry ashing - aqua regia digestion-CaC_2O_4 co-precipitation-repeated $Sr(NO_3)_2$ precipitation -3-week ^{90}Y ingrowth-repeated $Y(OH)_3$ and $BaSO_4/SrSO_4$ precipitation- $Y_2(C_2O_4)_3$ precipitation-beta counting (^{90}Y)	769	76.1 ± 7.7	0.131 ± 0.016	0.04	-10.1[#]	28.2[#]
	UH-Sr-II	Dry ashing – dissolution with 8 mol/l HNO_3-Sr column - $SrCO_3$ precipitation – 3-week ^{90}Y ingrowth – LSC (^{90}Y Cerenkov counting)	564	18%-97%	0.118 ± 0.009	0.04	-19.0[#]	26.5[#]
	IFE-Sr-II	Dry ashing - conc.HNO_3 dissolution-TBP extraction - $Y(OH)_3$ precipitation -$Y_2(C_2O_4)_3$ precipitation-beta counting (^{90}Y)	277	NA[$]	0.188 ± 0.026	0.017	29.1[#]	28.9[#]
	FOI-Sr-II	Microwave-assisted conc. HNO_3 digestion - Sr resin – LSC (^{90}Y Cerenkov counting)	24	81.2 ± 6.6	< LOD	60		
	Mean value ± sd				0.146 ± 0.037			

*The activity is calibrated to 15th Oct 2015. [#] Bias and P values are calculated using the mean value ± sd, for reference purpose only. [$]NA: not available.

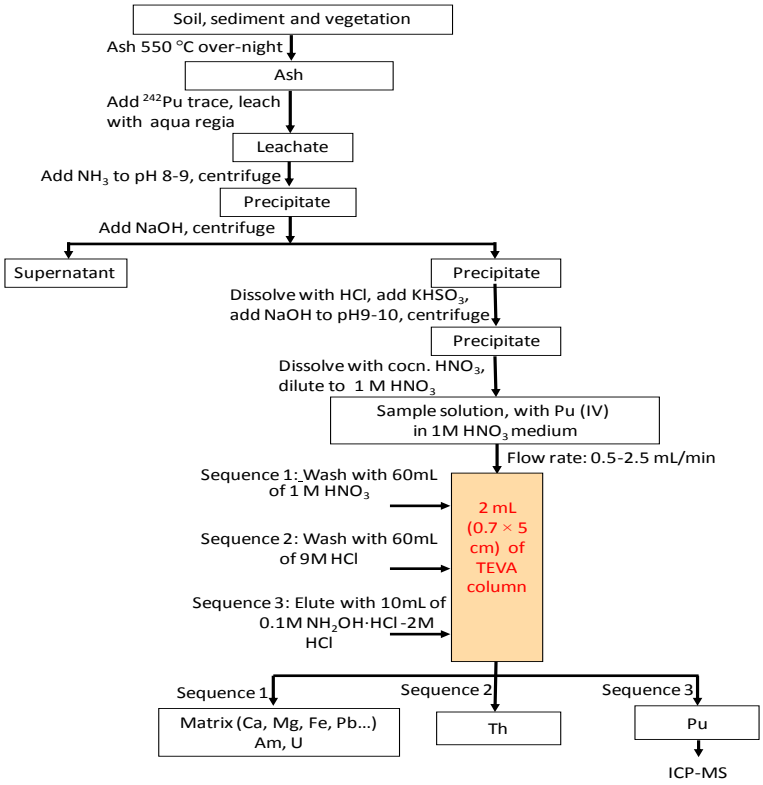

Figure. 1 Analytical procedure for Pu determination in DTU-Pu-II method

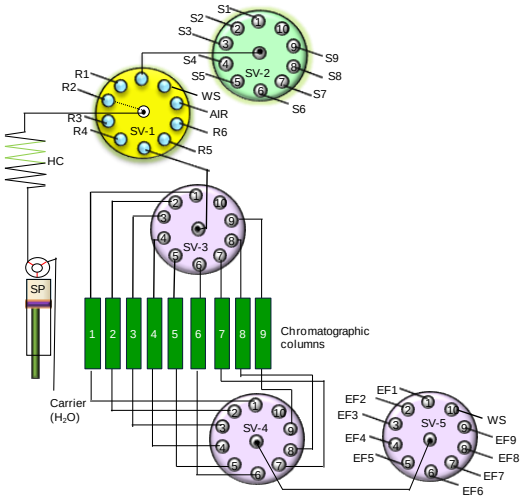

Figure. 2 Sequential injection steup for Pu determination in DTU-Pu-II method (SP: syringe pump, HC: holding coil, S1-S9: ports for sample loading, EF1-EF9: ports for eluate collection, WS: waste, AIR: port for air aspiration to isolation the carrier from the solution drawn into the holding coil, SV-1-SV-5: selective valves, R1-R6: reagents for column separation)

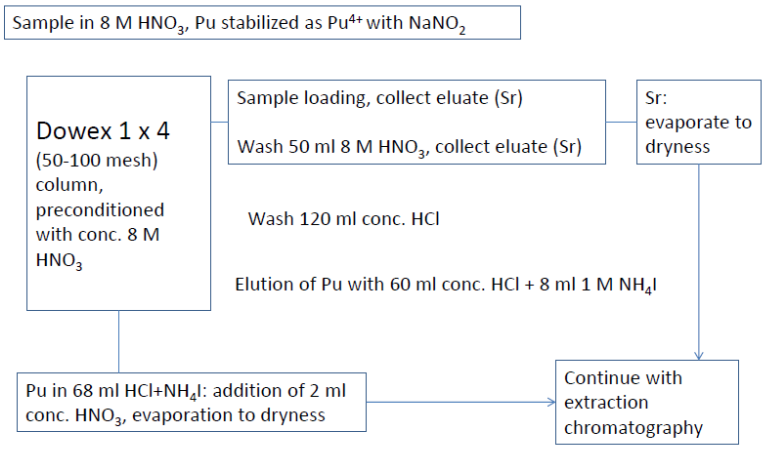

Figure 3. Chromatographic purification of Pu with Dowex 1x4 resin in UH-Pu-I method

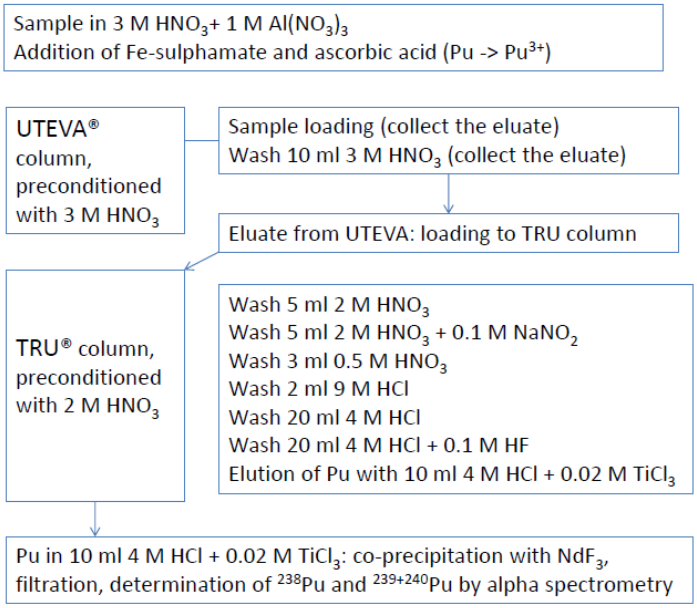

Figure 4. Chromatographic purification of Pu with UTEVA+TRU resins in UH-Pu-I method

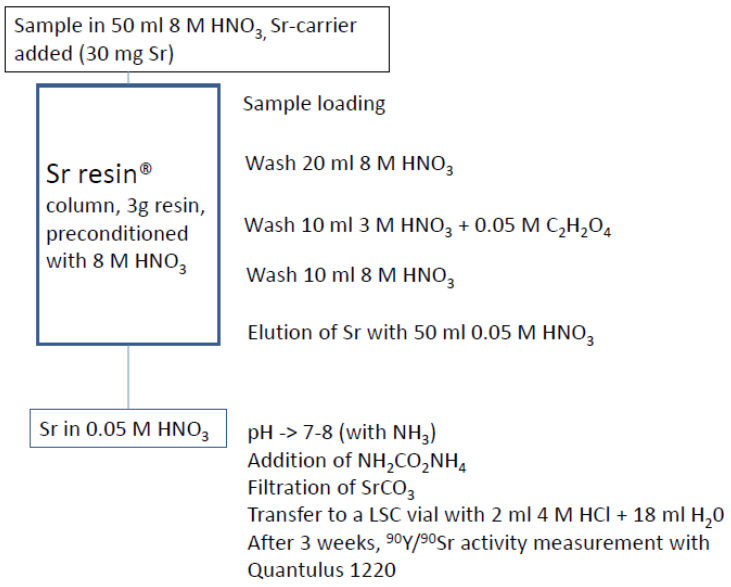

Figure 5. Chromatographic purification of ^{90}Sr with Sr-resin in UH-Sr-I and UH-Sr-II methods

Figure 6. $SrCO_3$ precipitations obtained after filtration in UH-Sr-I and UH-Sr-II methods for IAEA-TEL-no.5 soil. Three rust-colored precipitations (left) are the soil samples, two white-colored are blanks (right).

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Appendix I. Experimental record DTU-Pu-I method

Experimental record for NKS Rapid-tech inter-comparison in DTU-Pu-I method		
Sample ID	**Sample amount, g**	
IAEA-TEL no.5	10.0	
Stage 1. Pre-treatment		
Step no.	Detailed description of the operation	Duration (h)
1	Sample weighing Ashing at 550 °C Cooling	16
2	Tracer spiking Acid digestion Cooling	3
3	Filtration Washing with 0.2mol/LHCl	0.5
4	$Fe(OH)_3$ co-precipitation	1
5	Dissolve the sample with conc. HCl and dilute with H2O Add $K_2S_2O_5$, stir for 20 min. Adjust pH to 9 with NH3, centrifuge for 10 min at 3000 rpm	
6	Dissolve the sample in 8M HNO_3	
Stage 2. Column separation		
Step no.	Description	Duration (h)
1	Pack a 10 ml AG 1x4 column	6.5
2	Pre-condition the column with 20 ml 8 mol/l HNO_3 Flow rate: 1-2 mL/min	
3	Load the sample solution onto the AG 1x4 column Flow rate: 1 mL/min	
4	Wash the column with 200 ml 8 mol/l HNO_3 Flow rate: 1 mL/min	
5	Wash the column with 100 ml of 9 mol/l HCl Flow rate: 1 mL/min	
6	Eluate Pu with 100 ml 0.5mol/LHNO3 Flow rate: 1 mL/min	
Stage 3. Source preparation		
Step no.	Description	Duration (h)
1	Evaporate Pu eluate to dryness	1
2	Source preparation for ICP-MS	
Stage 4. Detection		
Step no.	Description	Duration (h)
1	Sample is measured on X-series ICP-MS	0.2
	Total	**28 h**

Appendix II. Experimental record for UH-Pu-I and UH-Sr-I method

Experimental record for NKS Rapid-tech inter-comparison UH-Pu-I and UH-Sr-I method		
Sample ID	**Sample amount, g**	(Three sub-samples were analyzed)
IAEA-TEL No. 5	10.131	
IAEA-TEL No. 5	10.0163	
IAEA-TEL No. 5	10.033	
Stage 1. pre-treatment		
Step no.	Detailed description of the operation	Duration (h)
1	Ashing in a muffle furnace at 450 ˚C overnight.	16
2	Leaching with conc. HNO_3 on a hot plate. H_2O_2 is added in a final stage to ensure the sample oxidation.	6
3	After cooling the sample, filtration through a glass fiber filter.	3
4	Solution evaporated to dryness.	16
5	Stabilization of Pu as Pu (IV) with $NaNO_2$, heating for 30 mins, then let cool for 1h.	1.75
Stage 2. Column separation		
Step no.	Description	Duration (h)
1	Anion exchange with Dowex 1 x 4 resin column. The first eluate contains Sr (will be collected), then the column is washed and finally Pu is eluted with conc. HCl + NH_4I mixture (will be collected).	7
2	Evaporation of Sr and Pu fractions collected from anion exchange separation.	7
3	Pu-fraction: Reduction and stabilization of Pu as Pu(III) with ascorbic acid and Fe-sulphamate.	0.25
4	Pu-fraction: Sample loading first to UTEVA column and then the eluate from UTEVA column to TRU column. Finally Pu is eluted from TRU column with 4 mol/l HCl + 0.02 mol/l $TiCl_3$.	6
5	Sr-fraction: Residue from anion exch. Is dissolved and loaded to a Sr-resin column. After washings, Sr is eluted with 0.05 mol/l HNO_3.	7
Stage 3. Source preparation		
Step no.	Description	Duration (h)
1	Pu-fraction: Co-precipitation of Pu with Nd-carrier and HF. Cooling in a refrigerator.	0.5
2	Pu-fraction: Filtration through a membrane filter.	0.25
3	Pu-fraction: Drying of the membrane filter, gluing to a plastic counting plate.	0.5
4	Sr-fraction: precipitation of Sr in $SrCO_3$. Heating, adjusting pH to 7-8, addition of $NH_2CO_2NH_4$. After cooling, filtration of $SrCO_3$ onto a membrane filter. Dry weight of the precipitation for Sr-yield determination. The filter with precipitation is transferred to a liquid scintillation vial, where HCl and H_2O is added.	2.5
6	Sr-fraction: waiting three weeks for a complete $^{90}Y/^{90}Sr$ equilibrium in the samples.	504 (3 weeks)
Stage 4. Detection		
Step no.	Description	Duration (h)
1	Pu: Measurement of ^{238}Pu and $^{239+240}Pu$ with Canberra's Alpha Analyst spectrometer (PIPS detectors).	168 (7 days)
	Sr: LSC measurement of $^{90}Y/^{90}Sr$ by Cerenkov counting with Quantulus 1220.	10
	Total for Pu	**216 h**
	Total for Sr	**564 h**

Appendix III. Experimental record for IFE-Pu-I method

Experimental record for NKS Rapid-tech inter-comparison in IFE-Pu-I method		
Sample ID	**Sample amount, g**	
IAEA-TEL no.5	10,03 before drying 9,98 g g after drying	
DS-1	9.56 g before drying 8.91 g after drying	
Stage 1. Pre-treatment		
Step no.	Detailed description of the operation	Duration (h)
1	Drying overnight at 105°C.	16
2	Ashing: – 660 min up to 450°C – 300 min at 450°C	16
3	Add 0.1 ml ^{242}Pu spike	7.5
4	Add 100 ml of Aqua Regia and heat it for 7h. Add H_2O_2. Evaporate to dryness. Add HF and HNO_3. Evaporate to dryness.	
5	Warm-up the solution and add 10g of oxalic acid. Increase the pH to 5-6 with NH_3 conc. Warm up the solution for ca. 1h.	1.5
6	Once the solution is cold, filter the solution though a Whatman 42 grade filter using a Buchner filter. Wash the beaker with a 10% oxalic acid solution	
7	Ashing: – 180 min up to 110°C – 720 min at 110°C – 180 min up to 450°C – 120 min at 450°C – 300 min up to 600°C – 720 min at 600°C	37
8	Dissolve the sample in HNO_3 conc. Evaporate to dryness	2
9	Dissolve the sample in 20 ml 3M HNO_3 – 0.1 mol/l sulfamic acid – 0.1 mol/l ascorbic acid	
Stage 2. Column separation		
Step no.	Description	Duration (h)
1	Set the columns in the following order (top - bottom): UTEVA-TRU-Sr and a 20 ml reservoir	2.5
2	Precondition the column with 20 ml 3 mol/l HNO_3. Flow rate: 1-2 mL/min	
3	Load the sample onto the columns and allow draining. Flow rate: 1 mL/min	
4	Add 10 ml 3 mol/l HNO_3.and allow draining. Flow rate: 1 mL/min	
5	Dimount the columns Throw the UTEVA column and continue with the TRU resin (the Sr resin will be used in the next procedure)	
6	Add 10 ml of freshly prepared 3 mol/l HNO_3 – 0.1 mol/l $NaNO_2$ and allow draining Flow rate: 1 mL/min	
7	Add 2 ml of 9 mol/l HCl and allow draining. Flow rate: 1 mL/min	
8	Add 20 ml 4 mol/l HCl and allow draining. Flow rate: 1 mL/min	
9	Ensure that a clean labeled container is placed under the column	
10	Add 10 ml 4 mol/l HCl + 0.2 ml 15 % $TiCl_3$ and eluate Pu in a 20 ml scintillation vial Flow rate: 1 mL/min	
Stage 3. Source preparation		
Step no.	Description	Duration (h)
1	Add 100 µL Ce^{III} solution (500 µg Ce/mL) and 2 ml HF 40 % to the solution and allow to sit for 30 min	0.7
2	Filter through a Resolve® filter and glue the filter on a steel disc	
Stage 4. Detection		
Step no.	Description	Duration (h)
1	Sample is measured on alpha detectors	220
	Total	**303 h**

Appendix IV. Experimental record for DTU-Pu-II method

Experimental record for NKS Rapid-tech inter-comparison in DTU-Pu-II method		
Sample ID	**Sample amount, g**	
DS-1	10.0	
Stage 1. Pre-treatment		
Step no.	Detailed description of the operation	Duration (h)
1	Sample weighing Ashing at 550 °C Cooling	16
2	Tracer spiking Acid digestion Cooling	3
3	Filtration Washing with 0.2mol/LHCl	0.5
4	$Fe(OH)_3$ co-precipitation, centrifuge Add NaOH to the precipitate, centrifuge	1
5	Dissolve the sample with conc. HCl and dilute with H2O Add $K_2S_2O_5$, stir for 20 min. Adjust pH to 9 with NH3, centrifuge for 10 min at 3000 rpm	
6	Dissolve the sample in 1mol/LHNO_3	
Stage 2. Automated column separation		
Step no.	Description	Duration (h)
1	Pack a 2 ml AG 1x4 column	2.5
2	Pre-condition the column with 20 ml 1 mol/l HNO_3 Flow rate: 2.5 mL/min	
3	Load the sample solution onto the TEVA column Flow rate: 1 mL/min	
4	Wash the column with 60 ml 1 mol/l HNO_3 Flow rate: 2.5 mL/min	
5	Wash the column with 40 ml of 9 mol/l HCl Flow rate: 2.5 mL/min	
6	Eluate Pu with 20 ml NH_2OH HCl-2 mol/l HCl Flow rate: 1 mL/min	
Stage 3. Source preparation		
Step no.	Description	Duration (h)
1	Evaporate Pu eluate to dryness	0.5
2	Source preparation for ICP-MS	
Stage 4. Detection		
Step no.	Description	Duration (h)
1	Sample is measured on X-series ICP-MS	0.2
	Total	**24 h**

Appendix V. Experimental record for UH-Pu-II method

Experimental record for NKS Rapid-tech inter-comparison UH-Pu-II method		
Sample ID	**Sample amount, g**	(Three sub-samples were analyzed in the same sample set)
DS-1	9,9987	
DS-1	10,0275	
DS-1	9,9808	
Stage 1. pre-treatment		
Step no.	Detailed description of the operation	Duration (h)
1	Ashing in a muffle furnace at 450 ˚C overnight.	16
2	Cooling to the room temperature.	3
3	Leaching with conc. HNO_3 on a hot plate. H_2O_2 is added in a final stage to ensure the sample oxidation.	6
4	The sample is allowed to cool into room temperature.	1
5	Filtration through a glass fiber filter.	0.5
6	Solution evaporated to dryness.	7
7	Reduction and stabilization of Pu as Pu(III) with ascorbic acid and Fe-sulphamate.	0.25
Stage 2. Column separation		
Step no.	Description	Duration (h)
1	Sample loading: first to UTEVA column and then the eluate from UTEVA column to TRU column. Finally Pu is eluted from TRU column with 4 mol/l HCl + 0.02 mol/l $TiCl_3$.	6
Stage 3. Source preparation		
Step no.	Description	Duration (h)
1	Co-precipitation of Pu with Nd-carrier and HF. Cooling in a refrigerator.	0.5
2	Filtration through a membrane filter.	0.25
3	Drying of the membrane filter, gluing to a plastic counting plate.	0.5
Stage 4. Detection		
Step no.	Description	Duration (h)
1	Measurement with Canberra's Alpha Analyst spectrometer (PIPS detectors)	168 (7 days)
	Total	**209 h**

Appendix VI. Experimental record for DTU-Sr-I method

Experimental record for NKS Rapid-tech inter-comparison DTU-Sr-I method		
Sample ID	**Sample amount, g**	
IAEA-TEL no.5	10.0	
Stage 1. Pre-treatment		
Step no.	*Detailed description of the operation*	*Duration (h)*
1	Ash the sample at 550°C overnight	16
2	Spike tracer, aqua regia digestion and cool	2.5
3	Filtration, wash with 0.2 mol/l HCl	0.5
4	Evaporate to 100 ml and $Fe(OH)_3$ precipitation until ^{85}Sr activity in the precipitate is less than 3% of the total ^{85}Sr activity spiked	5
5	Add NaOH to form $Ca(OH)_2$ precipitate, centrifuge Heat to boiling and add Na_2CO_3 to form $SrCO_3$ precipitate, heat for 1 h. Cool and centrifuge. Repeat $Ca(OH)_2$ and $SrCO_3$ precipitate one more time.	10
Stage 2. Purification		
Step no.	*Description*	*Duration (h)*
1	Add conc. HNO_3 to form $Sr(NO_3)_2$ precipitate twice, centrifuge Dissolve the $Sr(NO_3)_2$ precipitate with 50 mL. H_2O	505
2	Add 5 mg Fe^{3+} and then 6 mol/l NaOH to pH =10, centrifugation. Add 5 mg Y^{3+}, 1 mg Ba carrier and 1 ml 12 mol/l HCl to the supernatant.	
3	The sample was stand over 3 weeks for the ingrowth of ^{90}Y.	
Stage 3. Y precipitation		
Step no.	*Description*	*Duration (h)*
1	Add 25% NH_3 to pH >10 to form $Y(OH)_3$, centrifuge.	2
2	Dissolve $Y(OH)_3$ precipitate with 1 ml 6 mol/l HNO_3 Add 5 mg Sr^{2+} carrier. Repeat $Y(OH)_3$ precipitation again.	
3	Dissolve the $Y(OH)_3$ precipitate with 1 ml 6 mol/l HNO_3 and dilute to 20 ml with H_2O. Add 5 mg Ba^{2+}carier and 2 mg Sr^{2+} carrier. Add 1 ml 2 mol/l H_2SO_4 to form $BaSO_4/SrSO_4$ precipitation, centrifuge.	
4	Add 25% NH_3 to the supernatant to pH >10 to form the $Y(OH)_3$ precipitate.	
5	Repeat $BaSO_4/SrSO_4$ and $Y(OH)_3$ precipitation (step 3-4) again.	
Stage 4. Source preparation		
Step no.	*Description*	*Duration (h)*
1	Add 5 drops of 6 mol/l HNO_3 to dissolve the sample.	1
2	Add 20 ml 8% $H_2C_2O_4$. Filter the $Y_2(C_2O_4)_3$ with a filter paper and dry	
Stage 5. Detection		
Step no.	*Description*	*Duration (h)*
1	Measure the sample (including background and standard) by a low background gas flow Geiger Müller beta counter for a week	168
Stage 6. Yttrium Yield		
Step no.	*Description*	*Duration (h)*
1	After β-measurement, heat the filter at 550°C overnight	18
2	Dissolve the yttrium oxide in 0.5 HNO_3 and measure the concentration of stable Y by ICP-OES.	
	Total	**728**

Appendix VII. Experimental record for IFE-Sr-I method

Experimental record for NKS Rapid-tech inter-comparison IFE-Sr-I method		
Sample ID	**Sample amount, g**	
IAEA-TEL no.5	10.03 before drying, 9.98 g g after drying	
Stage 1. Pre-treatment		
Step no.	*Detailed description of the operation*	*Duration (h)*
1	c.f. Stage 1 of Analysis of plutonium in soil samples	80
Stage 2. Column separation		
Step no.	*Description*	*During (h)*
1	Continue with the Sr-resin used in Stage 2 / Step 5 of Analysis of plutonium in soil	337
2	Add 10 ml 8 mol/l HNO_3 and allow draining. Flow rate: 1 mL/min	
3	Add 5 ml 3 mol/l HNO_3 – 0.05 mol/l oxalic acid and allow draining. Flow rate: 1 mL/min	
4	Add 5 ml 3 mol/l HNO_3 and allow draining. Flow rate: 1 mL/min	
5	Note the date and time for the ingroing of Y	
6	Add 10 ml 0.05 mol/l HNO_3 and eluate Sr in a 20 ml scintillation vial. Flow rate: 1 mL/min	
7	Determine the Sr yield using the NaI detector	
8	Add 10 mg of Y-carrier and wait 14 days for Y ingroing	
Stage 3. Y precipitation		
Step no.	*Description*	*Duration (h)*
1	Check that the pH is around 1-2, adjust it with HCl if it is not the case	4
2	Transfer the solution in a centrifuge glass and wash the scintillation vials with deionized water. Heat the sample to 90°C	
3	Adjust the pH to 8 with NH_3. Add 6 drops of H_2O_2 and heat it for 1h	
4	After cooling down, centrifuge at 2000 rpm for 10 min	
5	Dissolve the precipitate in 3-4 drops of HCl conc. and dilute with deionized water	
6	Adjust the pH to 8 with NH_3 and heat the sample 10 min	
7	After cooling down, centrifuge at 2000 rpm for 10 min	
8	Re-do pts 5 to 7	
9	Dissolve the precipitate in 3 drops of HCl conc. and add 25 ml of deionized water	
10	Adjust the pH to 2-3 with NH_3, stir well	
11	Add 2 ml of 10 mg/mL Pb-carrrier Stir well before adding 2 ml of saturated Na_2SO_4 solution. Stir well and let the solution sit for 5 min	
12	Stir gently and filtrate the solution throught a membran filter. Throw the filter	
Stage 4. Source preparation		
Step no.	*Description*	*Duration (h)*
1	Warm up the solution to 90°C. Add 1 ml of saturated oxalic acid solution drop by drop. Stir well.	1
2	Adjust the pH to 2-3 with NH_3 conc. while stirring. Let the sample stand for 1h at 90°C.	
3	Cool down the sample and filtrate throw glass fiber GF/A filter.	
Stage 5. Detection		
Step no.	*Description*	*Duration (h)*
1	Sample is measured with Risø detectors.	116
Stage 6. Yttrium Yield		
Step no.	*Description*	*Duration (h)*
1	After β-measurement, heat the filter at 900°C for 90 min in a porcelain crucible.	1
2	Dissolve the yttrium oxide in 3 ml HNO_3 conc. and evaporate to dryness. In parallel, take 3 times 1 ml of Y-carrier (10 mg/mL); add 3 ml HNO_3 conc. and evaporate to dryness.	
3	Dissolve the samples in 20 ml acetate buffer solution (pH = 4.4) Add 1 drop of xylenorange	
4	Titrate with 0.01M EDTA.	
5	Calculate the Y yield	
	Total	**539 h**

Appendix VIII. Experimental record FOI-Sr-I method

Experimental record for NKS Rapid-tech inter-comparison FOI-Sr-I method		
Sample ID	**Sample amount, g**	
IAEA-TEL-no.5	0.9885	
Stage 1. pre-treatment		
Step no.	Detailed description of the operation	Duration
1 Preparation	1.1 Weighing of sample 1.2 Addition of yield tracer and LiBO 1.3 Drying of sample	5 min/sample 5 min/sample 1 h for a batch of samples
2 Fusion	2.1 Fusion 2.2 Cooling	15 min 45 min
3 Dissolution	3.1 Fusion into beaker filled with 100 ml 10% HNO3 3.2 Stirring and heating until dissolved 3.3 Add PEG2000 3.4 Evaporate to 50 ml	7 min/sample 1 h 3 min 1 h
4 Cooling	Allow sample to cool overnight	Approx. 16 h
5 Preparation before separation	5.1 Filter through Millipore 00M into 50 ml measuring flask 5.2 Add 48 ml konc. HNO3 to achieve ~7M	45 min 5 min/sample
6 Yield determination	Take a subsample (1 ml) to determine yield via ICP-OES measurement	5 min/sample
Stage 2. Column separation		
Step no.	Description	Duration
1 pre-condition of resin	1.1 Place 2x2ml resin cartridge on vacuum-box with a 75 ml column attached. 1.2 Condition resin with 10 ml 8M HNO3	5 min/sample 14 min
2 Sample loading	2.1 Load sample on the resin 2.2 Rinse the sample container with 2x5 ml 8M HNO3 2.3 Change to clean 25 ml column as a reservoir	75 min 10 min 1 min
3 Rinse	3.1 10 ml 8M HNO3 3.2 10 ml 3M HNO3-0.05M oxalic acid 3.3 10 ml 8M HNO3	10 min 10 min 10 min
4 Elute	Elute Sr-fraction with 15 ml 0.05M HNO3 into scintillation vial	15 min
5 Yield determination	Take a subsample (0.1 ml) to determine yield via ICP-OES measurement	5 min/sample
Stage 3. Detection		
Step no.	Description	Duration
1 Measure for Sr-89	Measure with Cherenkov counting on LSC to quantify any eventual Sr-89 in the sample	15 min/sample
No Sr89 detected, no further separation required for determination of Y-90, and subsequently Sr-90		
2 In-growth	Leave over night In-growth of Y-90 in sample	16 h
3 Measurement of Y-90	Measure with Cherenkov counting on LSC to quantify Y-90 in the sample	4 h/sample
Stage 5. Yield determination		
Step no.	Description	Duration
1 Yield determination	Measure amount of stable strontium in the two subsamples and compare.	During LSC measurement so no extra time is consumed
	Total	**44 h**

Appendix IX. Experimental record for DTU-Sr-II method

Experimental record for NKS Rapid-tech inter-comparison DTU-Sr-II method		
Sample ID	**Sample amount, g**	
DM-1	100.0	
Stage 1. Pre-treatment		
Step no.	*Detailed description of the operation*	*Duration (h)*
1	Ash the sample at 550 ^{0}C in oven for 3 days	72
2	Add ^{85}Sr tracer and 0.5 g $SrCl_2 \cdot 6\ H_2O$, digest the sample with 40 ml aqua regia at 150 ^{0}C for 30 min and 200 ^{o}C for 1 h, respectively.	2
3	Dilute the sample with water to 120 ml and filtered with GF/A filter paper. Add 30 ml 8% $H_2C_2O_4$ and 25% NH_3 to pH =7-10, centrifuge.	0.5
Stage 2. Purification		
Step no.	*Description*	*Duration (h)*
1	Dissolve the sample with 30 ml 14 mol/l HNO_3 Add fuming HNO_3 to a concentration of $HNO_3 \geq 14$ mol/l to precipitate Sr as $Sr(NO_3)_2$.	505.5
2	Repeat $Sr(NO_3)_2$ for two more times	
3	Dissolved $Sr(NO_3)_2$ precipitate with H_2O	
4	Add 5 mg Fe^{3} and then NaOH to pH =10, centrifuge	
5	Add 5 ml Y^{3+}, 1 mg Ba carrier and 1 ml 12 mol/l HCl to the supernatant.	
7	Let the sample stand over 3 weeks for the ingrowth of ^{90}Y.	
Stage 3. Y precipitation		
Step no.	*Description*	*Duration (h)*
1	Add 25% NH_3 to pH >10 to form $Y(OH)_3$, centrifuge.	2
2	Dissolve $Y(OH)_3$ precipitate with 1 ml 6 mol/l HNO_3 Add 5 mg Sr^{2+} carrier. Repeat $Y(OH)_3$ precipitation again.	
3	Dissolve the $Y(OH)_3$ precipitate with 1 ml 6 mol/l HNO_3 and dilute to 20 ml with H_2O. Add 5 mg Ba^{2+}carier and 2 mg Sr^{2+} carrier. Add 1 ml 2 mol/l H_2SO_4 to form $BaSO_4/SrSO_4$ precipitation, centrifuge.	
4	Add 25% NH_3 to the supernatant to pH >10 to form the $Y(OH)_3$ precipitate.	
5	Repeat $BaSO_4/SrSO_4$ and $Y(OH)_3$ precipitation (step 3-4) again.	
Stage 4. Source preparation		
Step no.	*Description*	*Duration (h)*
1	Add 5 drops of 6 mol/l HNO_3 to dissolve the sample.	1
2	Add 20 ml 8% $H_2C_2O_4$. Filter the $Y_2(C_2O_4)_3$ with a filter paper and dry	
Stage 5. Detection		
Step no.	*Description*	*Duration (h)*
1	Measure the sample (including background and standard) by a low background gas flow Geiger Müller beta counter for a week	168
Stage 6. Yttrium Yield		
Step no.	*Description*	*Duration (h)*
1	After β-measurement, heat the filter at 550°C overnight	18
2	Dissolve the yttrium oxide in 0.5 HNO_3 and measure the concentration of stable Y by ICP-OES.	
	Total	**769**

Appendix X. Experimental record for UH-Sr-II method

Experimental record for NKS Rapid-tech inter-comparison UH-Sr-II method		
Sample ID	**Sample amount, g**	(Three subsamples were analyzed in the same sample set.)
DM-1	149.97	
DM-1	142.10	
DM-1	122.42	
Stage 1. pre-treatment		
Step no.	Detailed description of the operation	Duration (h)
1	Ashing in a muffle furnace at 450 ˚C overnight. Only a small sample amount (~50 grams) could be ashed at once, to avoid boiling over. Therefore, three overnight ashing periods was needed for each subsample.	3 x 12 = 36 (effective ashing time in an oven), or 3 x 14 = 42 (cooling time between milk powder additions taken into account)
2	Dissolution of ash in 8 mol/l HNO_3, heating.	0.5
Stage 2. Column separation		
Step no.	Description	Duration (h)
1	Sample loading to Sr resin-column. After washings, elution of Sr with 0.05 mol/l HNO_3.	5
Stage 3. Source preparation		
Step no.	Description	Duration (h)
1	Precipitation of Sr in $SrCO_3$: Heating, adjusting pH to 7-8, addition of $NH_2CO_2NH_4$. After cooling, filtration of $SrCO_3$ onto a membrane filter. Dry weight of the precipitation for Sr-yield determination. The filter with precipitation is transferred to a liquid scintillation vial, where HCl and H_2O is added.	2.5
2	Sr-fraction: waiting three weeks for a complete $^{90}Y/^{90}Sr$ equilibrium in the samples.	504 (3 weeks)
Stage 4. Detection		
Step no.	Description	Duration (h)
1	LSC measurement of $^{90}Y/^{90}Sr$ by Cerenkov counting with Quantulus 1220.	10
	Total	**564 h**

Appendix XI. Experimental record for IFE-Sr-II method

Experimental record for NKS Rapid-tech inter-comparison IFE-Sr-II method		
Sample ID	**Sample amount, g**	
DM-1	97.41 g before drying 93.12 g after drying	
Stage 1. Pre-treatment		
Step no.	*Detailed description of the operation*	*Duration (h)*
1	Drying overnight at 105°C. (It runs over a week-end, so I suppose it could have been drying for less hours)	88
2	Add 20 mg Sr-carrier, 10 mg Y-carrier and 2 ml ^{85}Sr-spike	
	Ashing: – 300 min up to 500°C – 500 min at 500°C	13.5
	Break the sample with the use of a spatula and ashing again: – 30 min up to 500°C 120 min at 500°C.	2.7
4	Dissolve the sample in 50 ml 14M HNO_3.	
Stage 2. Solvent extraction		
Step no.	*Description*	*Duration (h)*
1	Prepare TBP by mixing an equivalent volume with 14 mol/l HNO_3 in a separation funnel .Throw the acid phase.	
2	Run a TBP extraction of yttrium using 2 time 50 ml of freshly prepared TBP (the yttrium is in the organic phase). Note the date and time.	1.5
3	Remove the yttrium from the organic phase by washing it with deionized water.	
4	Evaporate until ca. 10 ml (not to dryness!)	3
Stage 3. Source preparation		
Step no.	*Description*	*Duration (h)*
1	Warm up the sample to 90°C and adjust the pH to 8 with NH_3 conc. Centrifuge at 2000 rpm for 10 min. Throw the solution.	0.5
2	Dissolve the sample with 2 drops of HCl conc. and 15 ml deionized water.	
3	Warm up the solution to 90°C. Add 1 ml of saturated oxalic acid solution drop by drop. Stir well.	0.5
4	Adjust the pH to 2-3 with NH_3 conc. while stirring. Let the sample stand for 1h at 90°C.	
5	Cool down the sample and filtrate throw glass fiber GF/A filter.	0.5
Stage 4. Detection		
Step no.	*Description*	*Duration (h)*
1	Sample is measured with Risø detectors.	166
Stage 5. Yttrium Yield		
Step no.	*Description*	*Duration (h)*
1	After β-measurement, heat the filter at 900°C for 90 min in a porcelain crucible.	
2	Dissolve the yttrium oxide in 3 ml HNO_3 conc. and evaporate to dryness. In parallel, take 3 times 1 ml of Y-carrier (10 mg/mL); add 3 ml HNO_3 conc. and evaporate to dryness.	
3	Dissolve the samples in 20 ml acetate buffer solution (pH = 4.4) Add 1 drop of xylenorange	1
4	Titrate with 0.01M EDTA.	
5	Calculate the Y yield	
	Total	**277 h**

Appendix XII. Experimental record for FOI-Sr-II method

Experimental record for NKS Rapid-tech inter-comparison FOI-Sr-II method		
Sample ID	**Sample amount, g**	
DM-1	0.5086	
Stage 1. pre-treatment		
Step no.	Detailed description of the operation	Duration
1 Preparation	1.4 Weighing of sample 1.5 Addition of yield tracer 1.6 Addition of konc. HNO_3 1.7 Let sample react with acid Assemble vessels	5 min/sample 5 min/sample 5 min/sample 10 min 5 min/sample
2 Microwave digestion	2.1 Ramping 2.2 Hold 2.3Cooling	10 min 20 min 40 min
3 Preparation part 2	3.1 Disassemble vessels 3.2 Add 0.5 ml H_2O_2 to dissolve organic residue 3.3 Filter through Millipore 00M into measuring flask 3.4 Dilute sample to 20 ml with MQ	5 min/sample 2 min/sample 20 min 10 min
4 Yield determination	4.1 Take a subsample (0.1 ml, "before"-sample) to determine yield via ICP-OES measurement	5 min/sample
Stage 2. Column separation		
Step no.	Description	Duration
1 pre-condition of resin	1.1 Place 2ml resin cartridge on vacuum-box with a 25 ml column attached. 1.2 Condition resin with 5 ml 8M HNO3	5 min/sample 7 min
2 Sample loading	2.1 Load sample on the resin 2.2 Rinse the sample container with 2x2.5 ml 8M HNO3 2.3 Change to clean 25 ml column	20 min 10 min 1 min
3 Rinse	3.1 5 ml 8M HNO3 3.2 5 ml 3M HNO3-0.05M oxalic acid 3.3 5 ml 8M HNO3	5 min 5 min 5 min
4 Elute	Elute Sr-fraction with 15 ml 0.05M HNO3 into scintillation vial	15 min
5 Yield determination	Take a subsample (0.1 ml, "after"-sample) to determine yield via ICP-OES measurement	5 min/sample
Stage 3. Detection		
Step no.	Description	Duration
1 Measure for Sr-89	Measure with Cherenkov counting on LSC to quantify any eventual Sr-89 in the sample	15 min/sample
No ^{89}Sr required for detection, therefore no further separation performed for determination of Y-90, and subsequently Sr-90		
2 In-growth	Leave over night (In-growth of Y-90 in sample)	16 h
3 Measurement of Y-90	Measure with Cherenkov counting on LSC to quantify Y-90 in the sample	4 h/sample
Stage 4. Yield determination		
Step no.	Description	Duration
1 Yield determination	Measure amount of stable strontium in the two subsamples and compare.	During LSC measurement so no extra time is consumed
	Total	**24 h**

Bibliographic Data Sheet **NKS-368**

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Abstract
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Effective sample processing techniques are essential in radionuclide determination for emergency preparedness, environmental monitoring, nuclear decommissioning and waste management to achieve expedite analysis. In 2014, NKS-B Rapid-Tech project gathered scientists working in radiochemistry among Nordic countries and oversaw the problems and needs in developing effective radiochemical methods. Based on screening the current analytical methods for common radionuclides (e.g., Sr, actinides) assays in individual institute, challenges and future development were identified by each institute. Several consensuses through the screening have been summarized in the final project report (NKS-

336).

To practically evaluate the analytical benefit in application of novel sample processing techniques and to exchange experiences for improving radio-analytical methods used for different purposes in nuclear-related field, an inter-comparison exercise for determination of ^{90}Sr and Pu isotopes in environmental samples was performed in 2015 among the collaborative institutes. The results obtained from the inter-comparison exercise are evaluated and the analytical performance of different novel techniques are discussed and summarized in this report.

Key words Novel techniques, radiochemical analysis, Pu, Sr, inter-comparison, soil, milk